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Complete Specification
entitled (54) DISPERSING AGENTS

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Applicant (71) **IMPERIAL CHEMICAL INDUSTRIES LIMITED**

Actual Inventor (72) **GEOFFREY RICHARD ROTHWELL**

Related Art (56) Nil

The following statement is a full description of this invention, including the best method of performing it known to us:

This invention relates to dispersing agents and more particularly to alcohol-soluble anionic dispersing agents based on naphthalene sulphonic acid/formaldehyde condensation products.

Low molecular weight condensates of naphthalene sulphonic acids with formaldehyde are known dispersing agents and are described in, for example, "Surface Active Agents" by Schwarz and Perry, published 1949 by Interscience Publishers Inc., on pages 119-120. Their preparation is described in U.K. Specification No. 7137/1913. These condensates have a structure in which mono-sulphonated naphthalene nuclei are linked together by methylene groups, and they are normally used as the neutral sodium salts. These salts are water-soluble but insoluble in polar organic solvents such as the lower aliphatic alcohols. For certain purposes it is desirable to prepare dispersions of solds in polar organic solvents, a particular instance being the dispersion of dyestuffs or pigments in alcoholic media to provide printing inks. Such dispersions are prepared by milling the dyestuff or pigment in the alcoholic medium in the presence of a dispersing agent.

It has now been found that very effective dispersing agents for this purpose are ammonium and amine salts of naphthalene-2-sulphonic acid/formaldehyde condensates.

The salts are obtained simply by neutralising the free sulphonic acid form of the condensates with ammonia, a quaternary ammonium hydroxide or an amine, the product usually having a pH in the range 7.0 to 7.5. The salts are soluble in alcohols, particularly ethanol. Some of them are soluble in water and others again are soluble in mixtures of ethanol and water.

In addition to ammonia, any amine or quaternary ammonium hydroxide which is capable of forming a stable salt with the

sulphonic acid group may be used in preparing the compounds of the present invention. Suitable amines include primary, secondary and tertiary aliphatic amines, primary aromatic amines and their N-alkyl and N,N-dialkyl derivatives, cycloaliphatic amines, aralkylamines, alkanolamines, heterocyclic amines and ethylene oxide adducts of long chain fatty amines containing up to 18 carbon atoms such as cocoamine and tallow amine (cocoamine is a mixture of amines prepared from coconut oil fatty acids and contains a predominant amount of n-dodecylamine together with minor amounts of n-octyl, n-decyl, n-tetradecyl, n-hexadecyl, n-octadecyl and n-octadecenyl amines; tallow amine is a mixture of C₁₄ - C₁₈ n-alkyl and alkenyl amines derived from animal tallow fatty acids.)

As specific examples of amines which may be used there may be mentioned mono, di- and tri-methylamine and the corresponding ethylamines, isopropylamine, n-butylamine, tert butylamine, di-n-butylamine; aniline, N-methylaniline, N,N-dimethylaniline and the corresponding ethyl anilines, di-n-butylaniline, benzylamine, N,N-dimethylbenzylamine, 2-phenylethylamine, mono-, di- and tri-ethanolamine, morpholine, N-methylmorpholine, piperidine, cyclohexylamine, β -diethylaminoethanol, n-octylamine, n-dodecylamine and the adduct of cocoamine with, for example, 15 molecular proportions of ethylene oxide. As an example of a quaternary ammonium hydroxide which may be used there may be mentioned tetraethylammonium hydroxide.

The solubility of the salts in ethanol and in water varies according to the compound which has been used to form the salt. For example, the salts with cyclohexylamine, triethylamine, β -diethylaminoethanol and the adduct of cocoamine with 15 mols of ethylene oxide are soluble in both water and ethanol. Salts

prepared using n-octylamine or n-dodecylamine are soluble in ethanol but not to any great extent in water. It is a simple matter to select the salt-forming compound or mixture of compounds in order to obtain a salt having the desired solubility characteristics in the alcoholic or aqueous alcoholic solvent system being employed.

The preferred salt-forming compound is triethylamine.

According to a further feature of the invention there are provided finely divided dispersions of solids, especially pigments or dyestuffs, in organic or aqueous organic liquid media which contain therein a dispersing agent which is an ammonium or amine salt of a naphthalene-2-sulphonic acid/formaldehyde condensate as hereinbefore defined.

The said dispersions can be obtained by any of the conventional and well known methods of preparing dispersions. Thus the solid, the organic or aqueous-organic liquid medium and the dispersing agent may be mixed in any order and the mixture then subjected to a mechanical treatment to reduce the particle size of the solid, for example by ball milling, bead milling or gravel milling until the dispersion is formed. Preferably the mechanical treatment is carried out until the particle size of the solid is less than 20 microns and preferably less than 10 microns.

If desired the dispersion can contain other substances, such as natural or synthetic resins, which are conventionally present in dispersions of pigments or dye-stuffs in organic liquids, and which are soluble in the liquid.

Alternatively, the solid can be treated to reduce its particle size independently or in admixture with either the organic or aqueous-organic liquid or dispersing agent, and the other

ingredient or ingredients than added following which dispersion can be obtained by stirring the mixture.

It is preferred that the amount of dispersing agent in the dispersions is such as corresponds to between 5 and 150% by weight, and preferably between 40 and 60% based on the weight of the solid to be dispersed, and the dispersions preferably contain from 5 to 70% by weight of the solid based on the total weight of the dispersion.

The organic or aqueous-organic liquids used to prepare the said dispersions can be any such inert liquids in which the said dispersing agents are at least partly soluble at ambient temperatures and which are stable under the subsequent conditions of usage of the dispersion. If desired mixtures of organic or aqueous-organic liquids can be used. The preferred organic liquid is ethanol. Methanol is also satisfactory but is less preferred because of its toxicity, and its greater volatility whereby it presents a greater flammability hazard.

The pigments can be either inorganic or organic pigments, and can be of any of the recognised classes of pigments. As examples of inorganic pigments there may be mentioned zinc oxide, Prussian Blue, cadmium sulphide, iron oxides, vermillion, ultramarine and chrome pigments including chromates of lead, zinc, barium and calcium and the various mixtures and modifications thereof such as are commercially available as greenish-yellow to red pigments under the name primrose, lemon, middle, orange, scarlet and red chromes.

As examples of organic pigments there may be mentioned pigments of the azo, thioindigo, anthraquinone, anthanthrone, isodibenzanthrone or triphendioxazine series, vat dye pigments,

phthalocyanine pigments such as copper phthalocyanine and its nuclear halogenated derivatives and copper tetraphenyl and octaphenyl phthalocyanines, quinacridone pigments and lakes of acid, basic and mordant dyestuffs. Such pigments are described in, for example, the 3rd Edition of the Colour Index which was published in 1971 under the heading "Pigments" and in subsequent authorised amendments thereto. Preferred pigments are copper phthalocyanine and its nuclear halogenated derivatives. When the pigment is β -form copper phthalocyanine it may be the normal pigmentary form of the copper phthalocyanine or it may be crude copper phthalocyanine.

The dispersing agents of the invention are particularly valuable for the preparation of pigmentary dispersions of copper phthalocyanine directly from crude copper phthalocyanine.

The dyestuffs can be any of the recognised classes of dyestuffs such as are described in for example the 3rd Edition of the Colour Index. A preferred class of dyestuffs comprises Disperse Dyestuffs, the resulting dispersions being of value for the production of printed paper which is to be used in the process of transfer colour printing.

The dispersions of the invention are fluid or semi-fluid compositions containing the pigment or dyestuff in finely divided form, and can be used for any purpose for which dispersions of these particular solids are conventionally used. Thus the dispersions are of particular value in the manufacture of printing inks, by incorporating the dispersions with the other components conventionally used in the manufacture of such inks.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by

weight unless otherwise stated, the relationship between parts by weight and parts by volume being that of the kilogram to the litre.

Example 1

71.2 Parts of a naphthalene-2-sulphonic acid/formaldehyde condensate, in the form of an aqueous paste containing 71.3% of condensate, the remainder being water, are dissolved in a mixture of 38.3 parts of water and 21.4 parts of 92% alcohol,
or in 59.7 parts of water,
or in 59.7 parts of 92% alcohol,
or in any desired mixture of water

and alcohol to a sum of 59.7 parts. The pH of the solution is 0.4 to 0.7 at room temperature.

Triethylamine is slowly added to any of the above solutions until the pH is in the region 7.0 to 7.5. The amount of triethylamine required is generally from 28.3 to 29.1 parts. The resulting solutions of dispersing agent of known concentration are used as such.

Preparation of a Dispersion

38.5 Parts of a blue disperse dyestuff (C.I. Disperse Blue 35) are mixed with a solution comprising 23.1 parts of the triethylamine salt of a naphthalene-2-sulphonic acid/formaldehyde condensate, 16.9 parts of water and 75.5 parts of 92% ethanol. The mixture is placed in a 2 lb. Kilner jar together with 900 parts of Dorset Pea gravel and the jar is rotated in a horizontal position at 100 revolutions per minute for 16 hours. The particles of dyestuff in the dispersion then had an average particle size of less than 5/u. The dispersion was separated from the gravel by means of a sieve of Monel metal gauze of 1/8 inch square mesh.

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Preparation of a Printing Ink from the Dyestuff Dispersion

(a) 1 Part of ethyl cellulose N22 or 0.5 part of ethyl cellulose N200 is slowly added to 99 parts of the aqueous alcoholic dyestuff dispersion prepared as described above, whilst stirring with a Silverson stirrer.

(b) 20 Parts of a 5% solution of ethyl cellulose N22 in 92% ethanol or 20 parts of a 2.5% solution of ethyl cellulose N200 in 92% ethanol are added to 80 parts of the aqueous alcoholic dyestuff dispersion prepared as described above, whilst stirring with a Silverson stirrer.

Ethyl cellulose N22 and N200 both have an ethoxyl content of 47.5 to 49.9%. N22 has a viscosity of 22 centipoises when measured at 25°C. as a 5% solution by weight in a mixture of 80 parts by weight of toluene and 20 parts by weight of ethanol. N200 has a viscosity of 200 centipoises when measured under the same conditions.

Example 2

Preparation of a Pigment Dispersion

6.4 Parts of pigment (C.I. Pigment Green 7) are added to a solution comprising 1.6 parts of the triethylamine salt of a naphthalene-2-sulphonic acid/formaldehyde condensate (prepared as described in Example 1) and 12 parts of 92% ethanol in a cylindrical liquid-tight glass bottle having a capacity of about 60 parts by volume and containing 55 parts of 3 m.m. diameter glass beads. The bottle, secured in a suitable synthetic foam holder, is clamped between the jaws of a paint conditioner and mechanically shaken for 1 hour. The use of a paint conditioner in this way to simulate ball milling on the small scale is described by Orwig in Off. Dig. F.P.V.P.C. 1954, 26,830.

Preparation of a Printing Ink from the Pigment Dispersion

The dispersion and beads are transferred to a larger vessel using 44 parts of a solution comprising 40% of a maleic acid-modified rosin partially esterified with pentaerythritol and 60% of 92% ethanol. After thorough mixing, the dispersion is separated from the beads by means of nylon gauze. The resulting resin-containing pigment dispersion is a satisfactory printing ink.

Example 3

The procedure described in Example 2 was repeated using 6.4 parts of crude beta-form copper phthalocyanine in place of the 6.4 parts of C.I. Pigment Green 7, the shaking with glass beads using a paint conditioner being carried out for 5 hours.

An excellent dispersion and derived printing ink were obtained.

Example 4

Dispersions of the following dyestuffs were prepared by the method described in Example 1 (the numbers in brackets are the C.I. constitution numbers, where known) :-

C.I. Disperse Yellow 39
C.I. Disperse Yellow 3 (11855)
C.I. Disperse Yellow 119
C.I. Disperse Orange 1 (11080)
C.I. Disperse Orange 25
C.I. Disperse Red 15 (60710)
C.I. Disperse Red 11 (60215)
C.I. Disperse Red 60
C.I. Disperse Violet 1 (61100)
C.I. Disperse Blue 72
C.I. Disperse Blue 14 (61500)

Example 5

A solution of the triethylamine salt of a naphthalene-2-sulphonic acid/formaldehyde condensate in ethanol, water or ethanol-water prepared as described in the first part of Example 1 is evaporated to dryness in an oven at a temperature of approximately 70°C.

The dispersing agent is obtained as a sticky solid in quantitative yield, and can be used for the preparation of dispersions in the same way as the original solution, with similar results.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. The dispersing agents comprising the ammonium or amine salts of naphthalene-2-sulphonic acid/formaldehyde condensates.
2. The dispersing agents as claimed in claim 1 wherein the amine salt is the triethylamine salt.
3. The dispersing agents as claimed in claim 1 or claim 2 as hereinbefore particularly described, especially with reference to the foregoing Example 1.
4. The dispersing agents as claimed in claim 1 or claim 2 as hereinbefore particularly described, especially with reference to the foregoing Example 5.
5. A process for the manufacture of the dispersing agents claimed in claim 1 which comprises neutralising a naphthalene-2-sulphonic acid/formaldehyde condensate with ammonia, a quaternary ammonium hydroxide or an amine.
6. A process as claimed in claim 5 as hereinbefore particularly described especially with reference to the foregoing Example 1.
7. Compositions of matter comprising a finely divided dispersion of a solid in an organic or aqueous organic liquid medium containing dissolved therein a dispersing agent as claimed in any one of claims 1 to 3.
8. Compositions of matter as claimed in claim 7 wherein the particle size of the solid is less than 20 microns.
9. Compositions of matter as claimed in claim 7 or claim 8 wherein the amount of the solid is from 5 to 70% by weight based on the total weight of the composition.
10. Compositions of matter as claimed in any one of claims 7 to 9 wherein the amount of the dispersing agent is from 5 to

150% by weight based on the weight of the solid.

11. Compositions of matter as claimed in any one of claims 7 to 10 wherein the solid is a dyestuff.

12. Compositions of matter as claimed in claim 11 wherein the dyestuff is a disperse dyestuff.

13. Compositions of matter as claimed in any one of claims 7 to 10 wherein the solid is an inorganic pigment.

14. Compositions of matter as claimed in any one of claims 7 to 10 wherein the solid is an organic pigment.

15. Compositions of matter as claimed in claim 14 wherein the organic pigment is a phthalocyanine pigment.

16. Compositions of matter as claimed in any one of claims 7 to 15 wherein the organic liquid is ethanol.

17. Compositions of matter as claimed in any one of claims 7 to 12 and 14 to 16 as hereinbefore particularly described especially with reference to the foregoing Example 1.

18. Compositions of matter as claimed in any one of claims 7 to 12 and 14 to 16 as hereinbefore particularly described, especially with reference to the foregoing Examples 2 to 4.

19. A process for the manufacture of the compositions of matter claimed in claim 7 which comprises subjecting a mixture of a solid, an organic or aqueous-organic liquid medium and a dispersing agent as claimed in claim 1, to a mechanical treatment so as to reduce the particle size of the solid.

20. A process as claimed in claim 19 as hereinbefore particularly described, especially with reference to the foregoing Example 1.

21. A process as claimed in claim 19 as hereinbefore particularly described, especially with reference to the foregoing

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Examples 2 to 4.

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PHILLIPS ORMONDE AND FITZPATRICK
Attorneys for:-
IMPERIAL CHEMICAL INDUSTRIES LIMITED

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